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Microscopic Zero Valent Silver for Dye Removal in Wastewater

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In the present study the removal efficiency towards dyes of microscopic metal silver, produced with a sodium borohydride reduction, was tested. In absence of stabilizers the synthesis proved to be fast, with completion in less than 5 minutes and yield of 99.7 %. The product has micrometric dimensions, while when citrate is added in the reactor particle size is reduced to 10-100 nm and stability results highly increased. The removal efficiency was tested on two dyes, Methylene Blue (MB) and Bromophenol Blue (BPB) for the micrometric particles only. Both dyes are removed in less than 1 hour, with 94 % efficiency on MB and 90 % on BPB. The promising performances shown by our material, which are very good removal efficiency and the evidence of removing the dye by degradation rather than its adsorption, suggest the possibility to overcome the health risk posed by nanometric silver particles (AgNPs), obtaining a material which presents both catalytic and antibacterial properties plus an easier removal from the treated effluent.

1. Introduction

Nowadays industrial dyes are used in most manufacturing processes, especially in textile and polymer industry (Doble and Kumar, 2005). Since the complete consumption of the dye in the industrial process cannot be achieved (Peternel et al., 2007), large quantities of dye-contaminated wastewaters are discharged in the environment. The macroscopic result of this contamination is the colouring of the water body, but the main concern resides in the health threat, since many dyes are classified carcinogenic and mutagenic (Sima and Hasai, 2013). In addition, metabolites from incomplete microbial degradation (such as aromatic amines) present an higher toxicity than the parent compound (Almeida and Corso, 2014). For the aforementioned reasons, it is pivotal to improve the efficiency of the remediation technologies of such contaminants not only for decolourization, but for an effective transformation in harmless compounds. In the last years different remediation methodologies have been developed and tested, both chemical and biological. The latter proved to potentially promote complete mineralization of dyes (Caselatto et al., 2011, Tan et al., 2013), however Almeida and Corso (2014) reported an increase in toxicity if the process is incomplete. Among chemical remediation, Advanced Oxidation Processes (AOPs) and adsorption on porous materials (mesoporous carbon, metal oxides) showed good efficiency (Sima and Hasai, 2013, Peláez-Cid et al., 2016), but they present some downsides. Adsorption only results in a shifting of the contamination from the wastewater to the absorbent, thus introducing the need for further treatments. AOPs are highly effective (Tatarko et al., 1999) and in many cases do not use toxic materials, but operative costs are still significant and a long treatment time is required (Poblete et al., 2017). In last years, remediation technologies based on metal nanoparticles proved to be efficient and versatile in their application on many emerging contaminants (Ingle et al., 2014, Freyria et al., 2011). Not only nanoparticles can be applied to different AOPs (Minero et al., 2005, Minella et al., 2016) but can also be applied directly to groundwater via injection (Tosco et al., 2014). When facing a dye contamination, silver nanoparticles (AgNPs) are very promising as they present both catalytic (Sagitha et al., 2016) and antibacterial activity (Kumari et al., 2016), thus achieving not only the degradation of the dye but also inhibiting biological activity, usually obtained with UV and/or sonication (Naddeo et al., 2009), preventing the potential formation of toxic metabolites. At the present time, two chemical reduction methodologies for production of silver nanoparticles (AgNPs) are commonly applied: the first uses sodium borohydride (Song et

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al., 2009), the latter a phytosynthetic procedure with different plant extracts (Baiocco et al., 2016, Khodadadi et al., 2017). Both these procedures proved to yield materials with nanometric size and colloidal properties, although the small dimension provides a very high reactivity colloidal materials present also high mobility in the environment (Tiraferri et al., 2011). This particular feature, combined with the toxicity of metal silver results in a risk for human health of significant concern (Stensberg et al., 2011). The novelty of the approach examined in this study resides in synthetizing silver particles with sodium borohydride using a reagents stoichiometry which leads to particles which quickly aggregates in micrometric clusters, hence significantly reducing their mobility. The purpose of the study is then assessing if non-nanometric silver maintains a good removal efficiency towards dyes as already showed by iron nanoparticles (Comba et al., 2011).

2. Materials and methods

2.1 Silver particles production

Zero Valent Silver (ZVS thereinafter) particles were produced from Silver Nitrate (CAS 7761-88-8, purity >99 %), Sodium Borohydride (CAS 16940-66-2, purity >99 %) as reducing agent (RA) and Sodium Hydroxide (CAS 1310-73-2, pellets). The synthesis was carried out in a reactor under mechanical mixing, where the reactants were added sequentially as an $AgNO_3$ solution and a mixture of RA and Sodium Hydroxide. The same synthetic protocol was carried out adding citrate as stabilizer to reduce the size of the particles and increase their stability.

2.2 Silver particles characterization

A dimensional analysis with a DLS proved unfeasible for non-stabilized particles, given their fast aggregation in micrometric clusters, hence characterization was carried out with an optical stereo-microscope (Optika S-10-2L, magnification 10x) equipped with a digital camera for image acquisition. Dimensional analysis of the sonicated suspension was achieved with TEM analysis (JEM 3010 – JEOL) and ImageJ (Schneider et al., 2012). A Malvern Zetasizer Nano-Z DLS was used to characterize the particles produced with citrate as stabilizer. Chemical characterization of the micrometric particles (mZVS) surface (5-10 nm depth) was achieved by X-ray Photoelectron Spectroscopy (PHI Scanning X-ray Microprobe Al Kα radiation). The sample was in powder form and calibration was obtained on adventitious carbon at 284.6 eV.

2.3 Silver particles reactivity

Microscopic ZVS reactivity was tested on Methylene Blue (MB) and Bromophenol Blue (BPB) solutions in batch conditions, under indoor ambient light. MB degradation was carried out on a 5 mg L^{-1} solution with 10 mg of mZVS, while 25 mg L^{-1} BPB was degraded by 14 mg mZVS. The particles used were synthetized 24 hours in advance and thoroughly washed to remove any reactants residues which may alter the degradation. For the same reason a ‘control’ sample was produced for each test, where the dye was diluted with the water in which the particles were suspended after complete washing. The dye removal was assessed with a spectrophotometric analysis carried out with a Specord S600. In order to provide a good discussion of the results a test to exclude adsorption phenomena as responsible for the decolouration was carried out. Given the solubility of both dyes in organic solvents, an extraction in a 50% $MeOH/H_2O$ mixture in a sonication bath for 5 minutes was operated on the recovered particles from the previous experiments on MB and BPB. To increase the sensitivity, the volume of the extractant solution was lower (one tenth) with respect to the dye solution volume; analysis were carried out using a spectrophotometric method.

3. Results and discussion

3.1 Silver particles characterization

Synthesis of ZVS particles carried out in the absence of stabilizer yielded primary particles with size in the 150-250 nm which form aggregates (radii 0.1-0.8 mm) (Figure 1). AgNPs with size of 10-100 nm were obtained when citrate was added in the reaction medium, providing long term stability to the suspension. For the non-stabilized particles, focus of this study, two different phases can be identified: half of the product (phase 1) appears in the form of a black powder, which includes platelets with a metallic sheen (phase 2). From the high resolution XPS analysis of Ag(3d) presented in Figure 2 we identified the two main peaks at 368.39 eV and 374.40 eV, and two satellite peaks at 372.19 eV and 377.75 eV. Both the energies of the main peaks and the presence of the satellite peaks are related to the presence of ZVS (Ferraria et al., 2012, Briggs, 1981), the slight shift in energies is due to the small dimensions of the particles, though in aggregated form. Further proofs supporting our claim derive from the peaks bandwidth (FWHM), we observed an average value of 0.97 eV which can be compared to the literature (Ferraria et al., 2012). All the silver salts presents FWHM higher than 1.2 eV, hence the observed value of 0.98 eV corresponds very likely to Ag(0) (FWHM 1.0÷1.2

eV). Moreover, from the stoichiometry used in preparing and mixing the reagents we expected a complete conversion of $AgNO_3$, confirmed by absence of Ag precipitation with addition of more RA or NaCl 5 M. The experimental yield, assuming only Ag(0) is formed, resulted to be 99.7 %. If some oxides were formed, a yield significantly higher than 100 % was to be expected. The difference in morphology between the two phases can be attributed to crystalline and amorphous ZVS.

Our material is then expected to maintain the property shown by metal silver to release Ag^+ ions (Chernousova and Epple, 2013), which are accounted responsible for the antibacterial properties (Stensberg et al., 2011). At the same time the removal of ZVS after the treatment of the contaminated effluent is facilitated by the micrometric size of the particles. Usually AgNPs have sizes below 50 nm, hence even a 0.02 μm pore-size filter would be unable to remove them. Our material can be removed with a 0.45 μm pore-size filter even after hours of moderate stirring, since it still maintains micrometric size. This have a significant influence on their environmental mobility as well (Icardi et al., 2014) in case of an application for groundwater remediation.

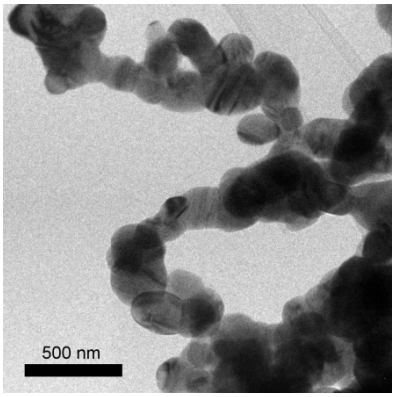

Figure 1: TEM imaging of freshly synthetized primary mZVS particles, after probe-sonication of the aggregates

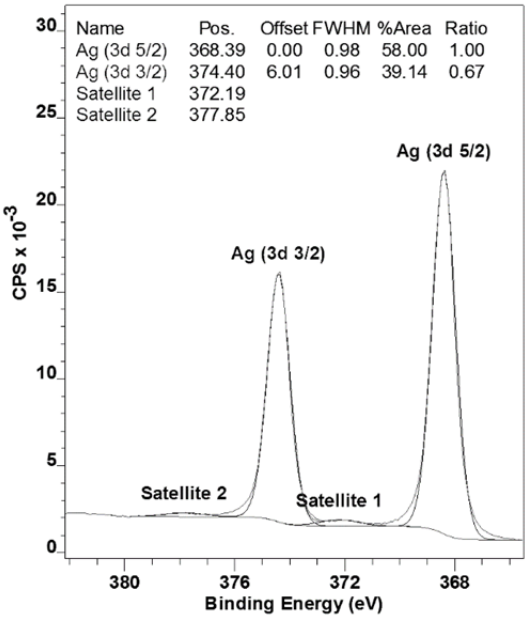

Figure 2: XPS analysis and peak deconvolution on non-pelleted mZVS for Ag(3d)

3.2 Silver particles reactivity

Both the dyes tested are removed by our material, as shown in Figure 3. Methylene Blue removal (Figure 3-left) by mZVS occurs in a relative short time with good efficiency; we determined a 94 % decolourization in less than 1 hour. Since the degradation is not complete we were also able to determine the removal capacity

(Φ^{MB}), which results to be 1.7 mg_{DYE} g_{mZVS}^{-1}. From our tests on BPB, mZVS showed a slightly lower decolourization, from the data reported in Figure 3-right 90 % efficiency is reached in less than 1 h; again we were able to determine the removal capacity (Φ^{BPB}), which results to be 6.4 mg_{DYE} g_{mZVS}^{-1}.
In both cases the 'control' sample showed a concentration stable at the initial value (C_0) over more than 4 h, hence degradation is operated by mZVS only.
Assuming a pseudo-first order kinetic, using an exponential fit which takes in account the incomplete degradation according to Equation (1), we are able to determine the value for the observed kinetic constant k_{obs}:

$$y = y_0 + A \cdot e^{-k_{obs} \cdot t} \quad (1)$$

From the data obtained the k_{obs} results to be 0.159 min^{-1} for MB and 0.144 min^{-1} for BPB. To compare the two constants we must take in account that we used different quantities of mZVS. If we normalize the k_{obs} for mass of nanoparticles used we obtain $k'_{obs}{}^{MB}$ = 0.0159 mg_{mZVS} min^{-1} and $k'_{obs}{}^{BPB}$ = 0.0103 mg_{mZVS} min^{-1}.
Although decolourization is very high, the driving mechanism can consist of adsorption rather than degradation, which according to our premises is undesired. In Figure 4-left the spectrum of the unprocessed MB is compared with the recovered fraction from mZVS. Assuming all the dye was recovered, it emerges that about one fourth of the removed dye is adsorbed (24.5 %) on the particles, while the remaining (75.5 %) appears to be degraded (data reported in Figure 4-right). Despite a slightly lower decolourization efficiency than on MB, on BPB the process appears to consist in degradation only (or at least with a negligible adsorption contribution) as the spectrophotometric analysis of the extract from the recovered particles produced only background noise (spectrum not showed).

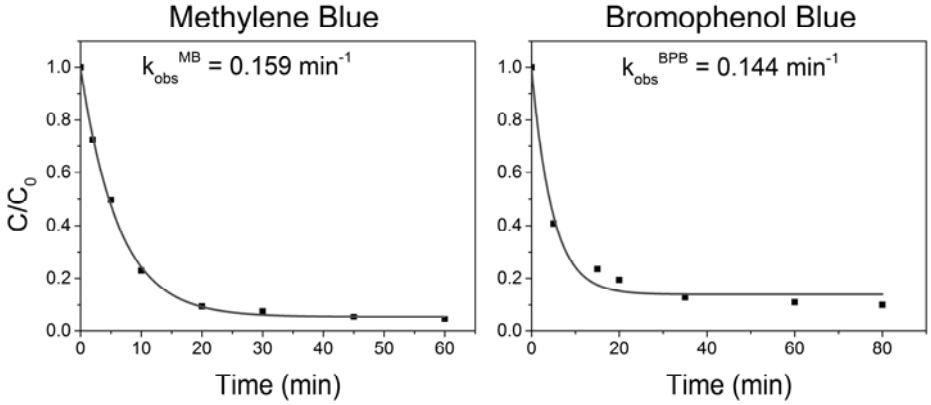

Figure 3: Degradation kinetics for MB using the peak at 663 nm (left) and BPB using the peak at 590 nm (right); kinetic constant obtained according Equation (1)

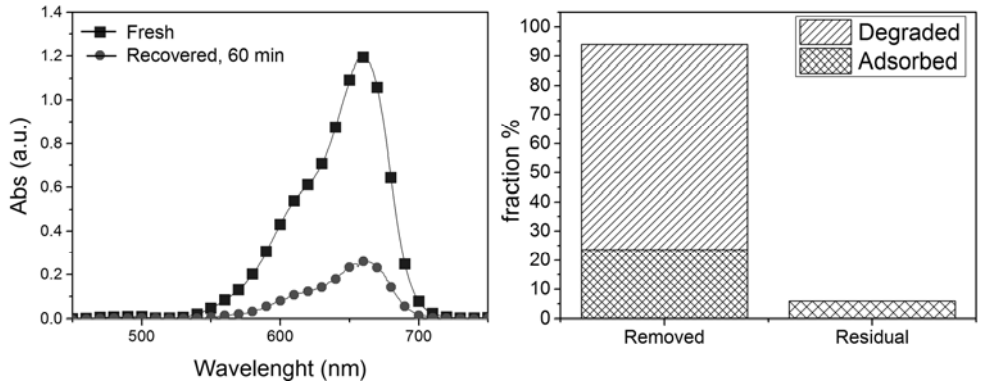

Figure 4: Absorbance of the unprocessed MB dye and the recovery from mZVS (left) and separation of decolourization in adsorption and degradation (right)

Our results are very promising, showing a decolourization driven mainly by degradation. On MB we found evidence of a partial absorption, while previous studies by Vanaja et al. (2014) with 10 mg phytosinthetized AgNPs showed 95 % decolourization in 72 hours on 10 mg L-1 MB. Whereas capable of degrading about half

of the dye for the same particle mass, mZVS presents a much faster kinetic than AgNPs achieving 94 % degradation after only 1 hour. Moreover, nanoparticles are commonly removed by flocculation, which requires additional chemicals and produces high quantities of sludge; with micrometric particles filtration may suffice for good removal of the material. For our tests on BPB, although they evidenced a slightly lower dye removal (90 %) than on MB an higher removal capacity equals 6.4 $mg_{DYE}\ g_{mZVS}^{-1}$ is observed. If compared with previous studies testing adsorbents (El-Gamal et al., 2015) which reports removal lower than 80 % in 72 minutes and an adsorption capacity of 5-107 $mg_{DYE}\ g_{ADS}^{-1}$ our product reached higher efficiency in less time, and the main process appears to be degradation. In addition, our material was tested under indoor ambient light and not direct sunlight or near-UV irradiation, which are expected to further improve its catalytic properties.

4. Conclusions

The devised synthetic protocol proved to be fast, with completion in less than 5 minutes, occurs in non-degased triple distilled water at room conditions and produces micrometric aggregates of AgNPs, with a 99.7 % yield. The washed materials can be reduced to nanometric size by means of probe sonication to particles with a diameter (obtained by TEM analysis) between 150-250 nm. Our material showed good decolourization performances on both MB and BPB, with 94 % and 90 % efficiency respectively and can be compared with some of the materials studied in previous literature.

The material obtained is also expected to release Ag^{+} ions in solution, thus providing antibacterial activity in the contaminated effluent during the remediation process. This is of paramount importance for those pollutants which metabolites present an higher toxicity, such as azo-dyes: inhibiting microbial communities can prevent such toxification. It is also important to notice that mZVS maintains micrometric size even after many hours of stirring, and nanometric particles are only obtained after probe-sonication. This means that separation will still be facilitated at the end of the remediation process.

In conclusion, the present study provides evidences on the good performance of aggregated nanometric silver, as it proved to maintain very high removal efficiency on dyes. Moreover, this decolourization appears to mainly consist in degradation rather than adsorption, hence it does not merely shift the pollutant from the wastewater to the adsorbent. Consisting in metal silver, the material also maintains the antibacterial properties which can be helpful in preventing toxification of the contaminants by microbial activity. Thanks to such properties such material can also be incorporated in membranes for reducing bio-fouling (Scannapieco et al., 2015) with less concern for a release in the environment. At the same time, thanks to its dimensions, the recovery of the material from a decontaminated effluent is significantly facilitated, reducing the risk for human health and its regeneration.

Although further studies will be needed on other pollutants, including azo-dyes, and testing the antibacterial activity micrometric silver could be used instead of nanometric silver particles in the remediation of contaminated effluents.

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